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# Computational Modeling of Uranium Corrosion and the role of Impurities(Fe, Cr, Al, C and Si)

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# Computational Modeling of Uranium Corrosion and the role of Impurities(Fe, Cr, Al, C and Si)

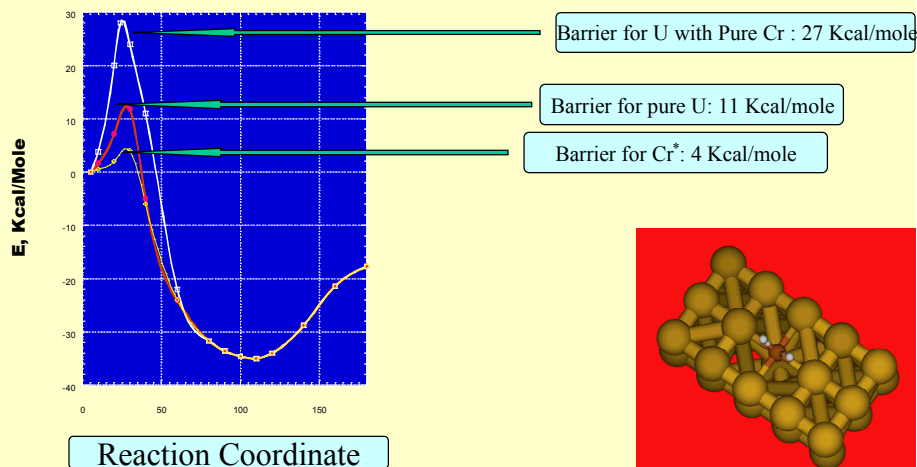
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My talk will focus on our recent computational modeling results of uranium corrosion and the impact of impurities on uranium corrosion, which occurs primarily through hydriding. Uranium hydriding is one of the most important processes that has received considerable attention over many years. Although significant number of experimental and modeling studies have been carried out concerning thermo chemistry, diffusion kinetics and mechanisms of U-hydriding, very little is known about the electronic structure and electronic features that govern the U-hydriding process. Our modeling efforts focus the electronic feature that controls the activation barrier and thus the rate of hydriding. Our recent efforts have been focused on the role of impurities such as Fe, Cr, Si, C, Al and so on. Moreover the role of impurities and the role of the product  $\text{UH}_3$  on hydriding rate have not been fully understood. Condon's diffusion model was found to be in excellent agreement with the experimental reaction rates. From the slopes of the Arrhenius plot the activation energy was calculated as 6.35 kcal/mole. Bloch and Mintz have discussed two models, one, which considers hydrogen diffusion through a protective  $\text{UH}_3$  product layer, and the second where hydride growth occurs at the hydride-metal interface. These authors obtained two-dimensional fits of experimental data to the pressure-temperature reactions. Powell et al. have studied U-hydriding in ultrahigh vacuum and obtained the linear rate data over a wide range of temperatures and pressures. They found reversible hydrogen sorption on the  $\text{UH}_3$  reaction product from kinetic effects at 21 °C. This demonstrates restarting of the hydriding process in the presence of  $\text{UH}_3$  reaction product. DeMint and Leckey have shown that Si impurities dramatically accelerate the U-hydriding rates.

We report our recent results of relativistic computations that vary from complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDCI) computations that included up to 60 million configurations for modeling of uranium-hydriding with cluster models will be presented. Our computed potential energy surface for the insertion of a U site into H<sub>2</sub> reveals that pure U site has to surpass a barrier of 20.9 kcal/mole for the U-hydriding. Once the barrier is surpassed a stable product is formed which is 22.4 kcal/mole more stable than the reactants. We have also developed a computational model to study the role of the UH<sub>3</sub> product and other impurities such as Fe, Cr, Si, C, Al, etc., on the uranium hydriding reaction. Our model reveals that the product UH<sub>3</sub> is highly ionic and thus U transfers electron density to the three hydrogens resulting in a U<sup>+3</sup> state. U<sup>+3</sup> is shown to insert into H<sub>2</sub> spontaneously thus demonstrating the U-site in the product UH<sub>3</sub> binds to H<sub>2</sub> spontaneously forming a complex in which H<sub>2</sub> is separated far enough so as to cause liberation of H atoms in the presence of U. Our computed potential energy surfaces reveal a 21 kcal/mole activation energy barrier for pure U reaction with H<sub>2</sub>. However, the presence of the product UH<sub>3</sub> catalyzes the U-hydriding. We have also modeled the presence of Si impurities for the U-hydriding reaction to show that the activation barrier is lowered by the presence of Si. However carbon impurity does not influence the hydriding process. Our computations reveal an electron donor-acceptor model for the U-hydriding, where H<sub>2</sub> exchanges electronic density from its occupied 1σ<sub>g</sub> orbital to the U(6d σ) orbital and back donation from the U(6d π) orbital back to H<sub>2</sub> 1σ<sub>u</sub> antibonding orbital. As seen from the figures shown below our recent works show that elemental impurities such as Al do not have impact on hydriding, elements such as Fe and Cr have small impact while the elemental carbon inhibits corrosion through the formation of ionic uranium carbide species.

### U+Cr

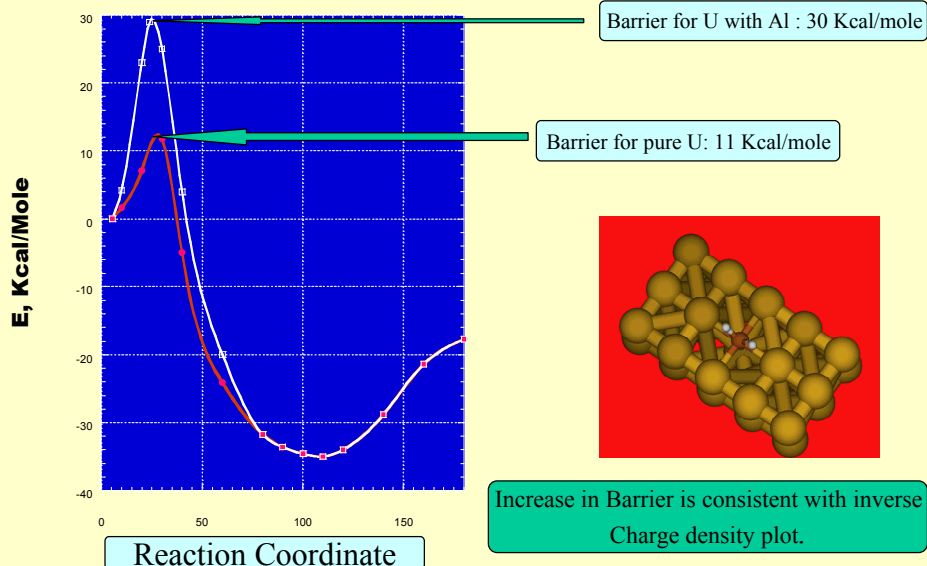
Although pure Cr by itself increases the activation energy  
Barrier excitation to  $\text{Cr}^*$  by other elements through overlap  
Decreases the barrier to only 4 kcal/mole.



Although pure elemental Cr does not initiate hydriding other impurities which can excite  
Cr to  $\text{Cr}^*$  through overlaps lowers the activation energy significantly.

### U+Al

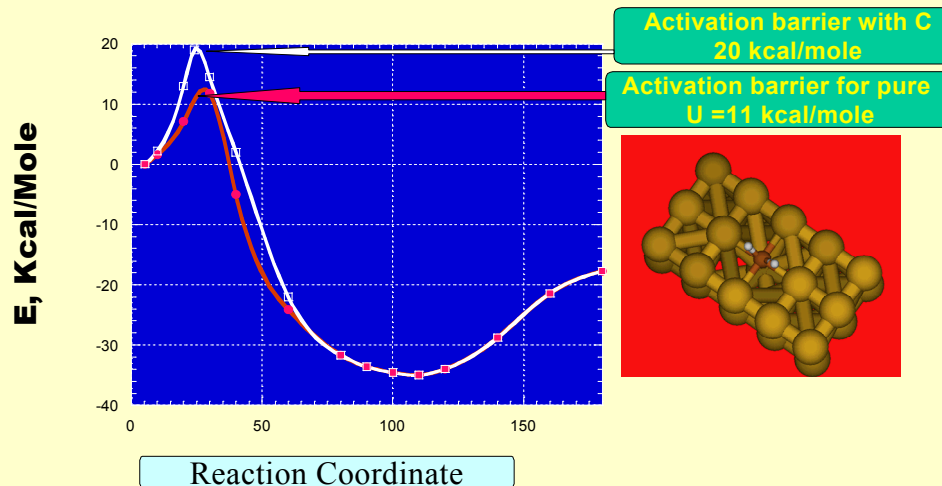
Al impurities increase the activation barrier for U-hydriding  
from 11 Kcal/mole to 30 Kcal/mole.



Increase in Barrier is consistent with inverse  
Charge density plot.

U+C

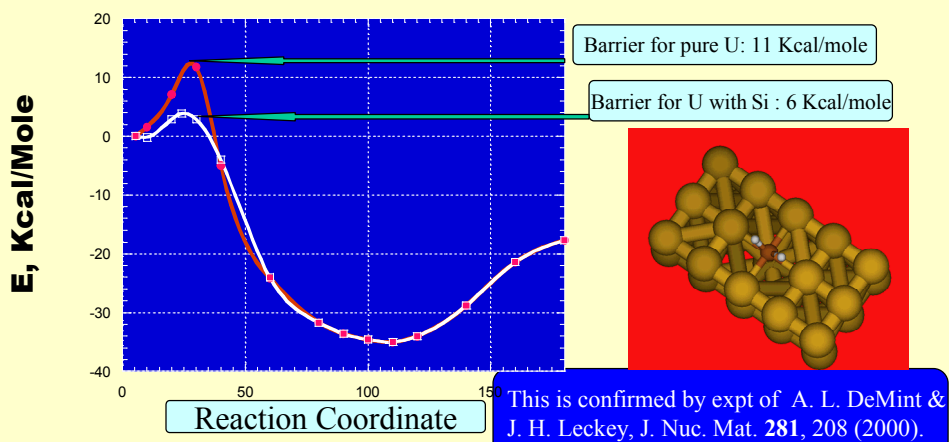
C impurities increase the activation barrier for U-hydriding from 11 Kcal/mole to 20 Kcal/mole.



We can apply this technique to screen other impurities for their hydride initiating potential.

U+Si

Si impurities lower the activation barrier for U-hydriding from 11 Kcal/mole to 6 Kcal/mole.

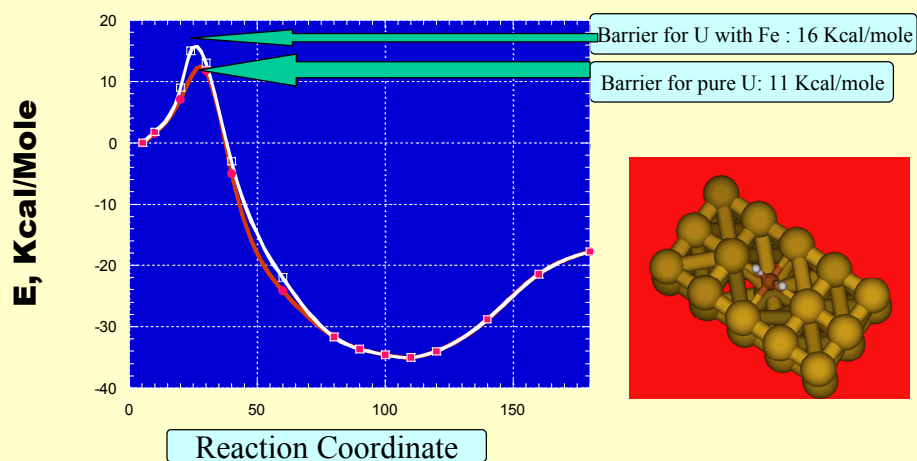


This is confirmed by expt of A. L. DeMint & J. H. Leckey, J. Nuc. Mat. **281**, 208 (2000).

We can apply this technique to screen many impurities for their hydride initiating potential.

U+Fe

Fe impurities increase the activation barrier for U-hydriding  
from 11 Kcal/mole to 16 Kcal/mole.



We can apply this technique to screen other impurities such as Cr, Ni, Al for  
their hydride initiating potential.